

Discontinuous methods for accurate, massively parallel quantum molecular dynamics: Lithium ion interface dynamics from first principles

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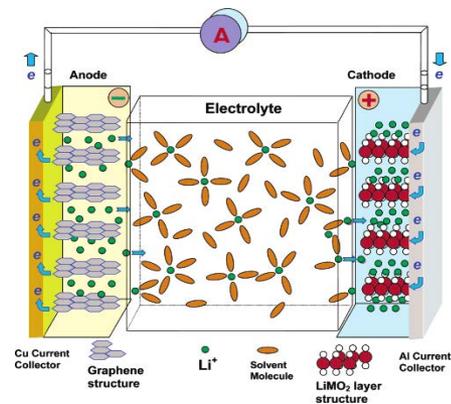
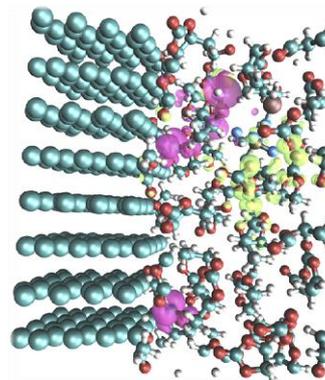
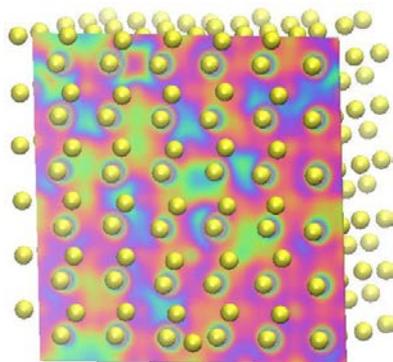
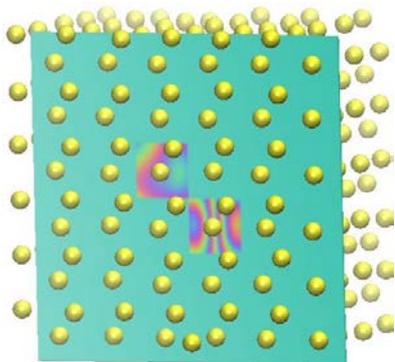
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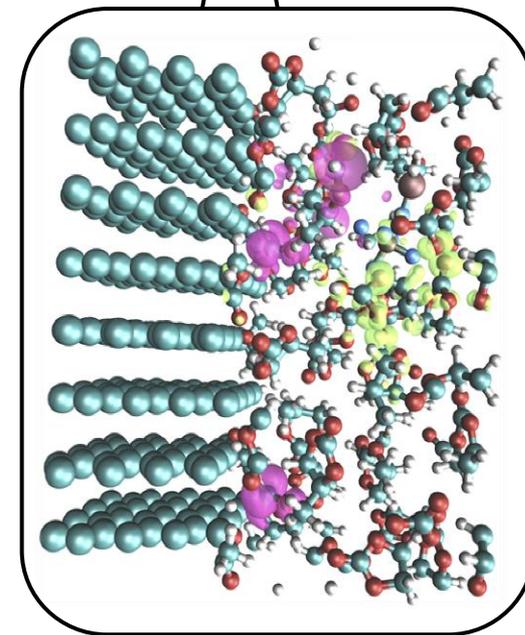
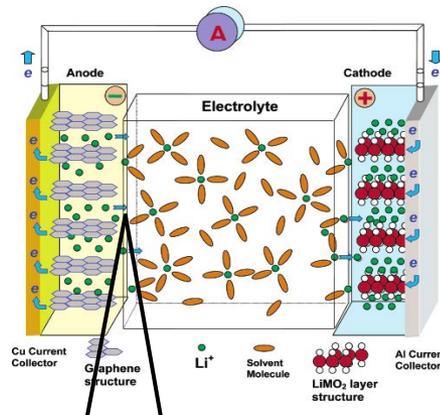
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Overview

- Li-ion batteries have revolutionized consumer electronics and have the potential to do the same for transportation (e.g., plug-in hybrids, all-electrics) and electrical distribution (e.g., load leveling)
- To do so, energy/power density, lifetime, safety must be increased
- Key issue: **solid-electrolyte interphase (SEI)** layer at electrolyte-anode interface, product of electrolyte decomposition
- Understanding has been hindered by need for both quantum mechanical description and sufficiently large length/time scales to capture necessary complexity
- In this work, we:
 - **Develop** new **Discontinuous Galerkin (DG)** electronic structure method to accomplish **quantum molecular dynamics (QMD)** on an unprecedented scale
 - **Apply** new method to advance understanding of the **structure and dynamics of electrolyte/SEI/anode systems**



QMD snapshot of SEI layer in Li-ion cell

Scientific questions

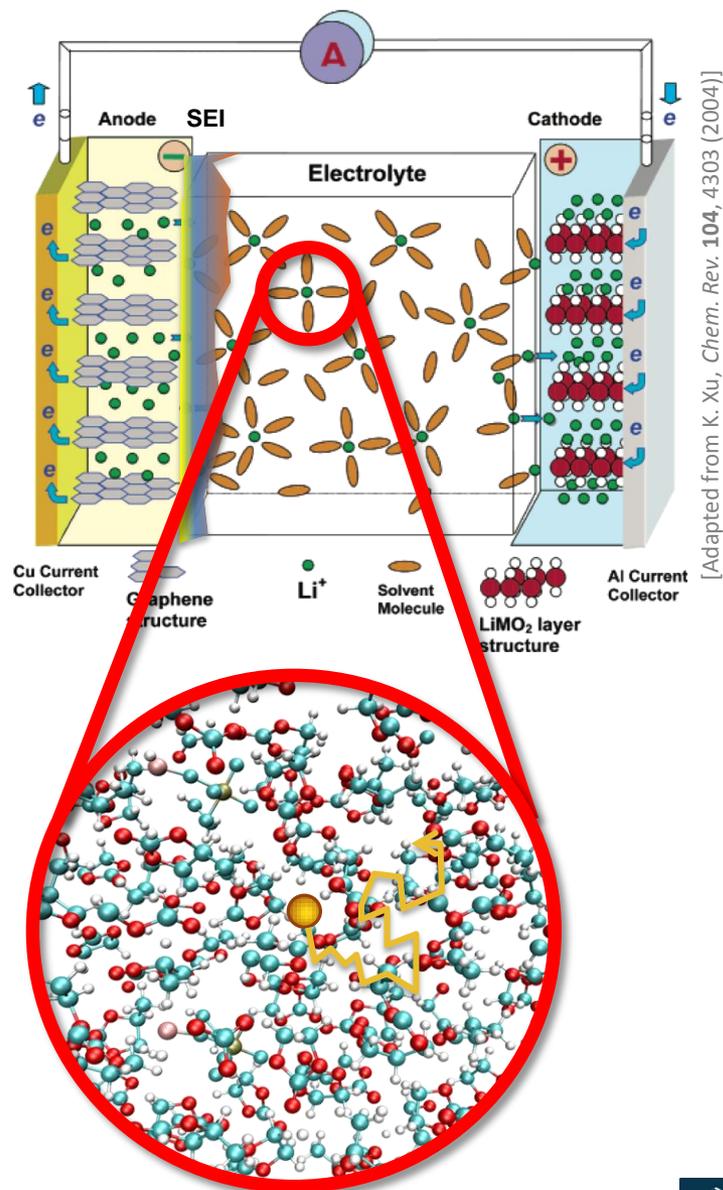
- What are the chemical mechanisms of **SEI formation**?
- How does the **composition of the electrolyte** affect interface/interphase reactivity and mass transport to the interface?
- How does the **molecular structure of the electrolyte** change near the anode interface and affect SEI formation and evolution?
- What **fundamental chemical insights can be used for future design** of electrolyte/anode systems, from knowledge of the mechanism of SEI formation and the relation to electrolyte structure, dynamics, and interface reactivity?



Simulations

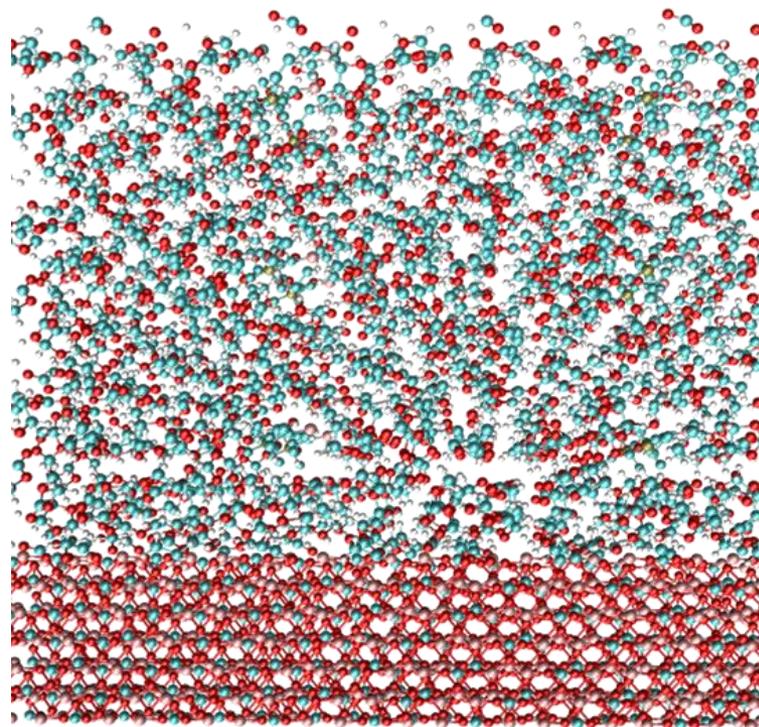
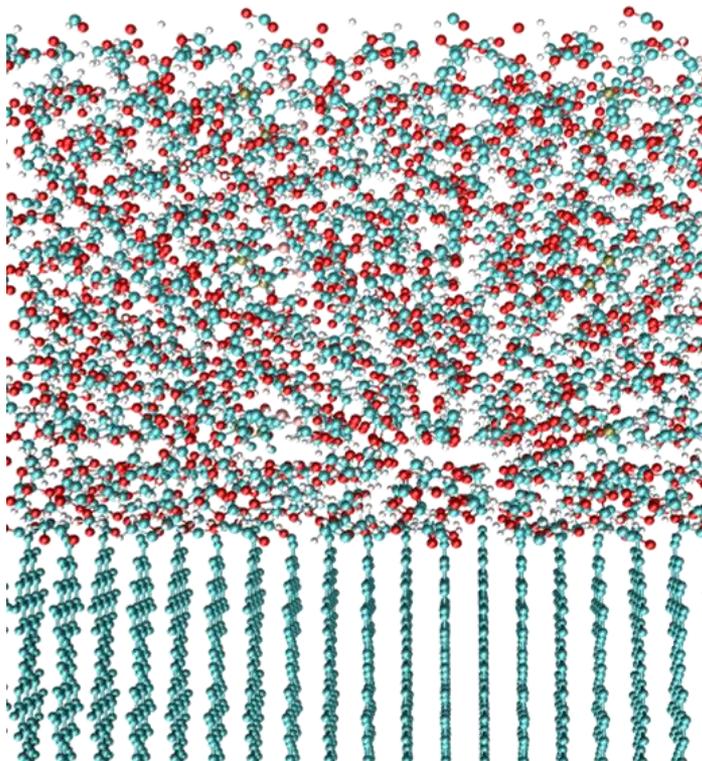
- Initial phase of project, while new DG code is developed and optimized: **Qbox** [1] for systems of < **1,000 atoms**
- Li^+ solvation and diffusion: determine diffusion coefficients, effect of counter-ion, differences in bulk vs near interface

Molecular dynamics simulation of 50/50 ethylene carbonate/propylene carbonate electrolyte



Simulations

- As the new DG method and code ramp up, we transition to it for larger scale simulations, up to **10,000 atoms and more**
- Full electrolyte-anode and electrolyte-SEI systems



EC/PC mixture (+ LiPF₆) on graphite (left) and Li₂CO₃ (right), used to study chemical reactions on the anode surface (for initial SEI formation) and a representative SEI compound (for SEI growth/evolution)

Quantum molecular dynamics (QMD)

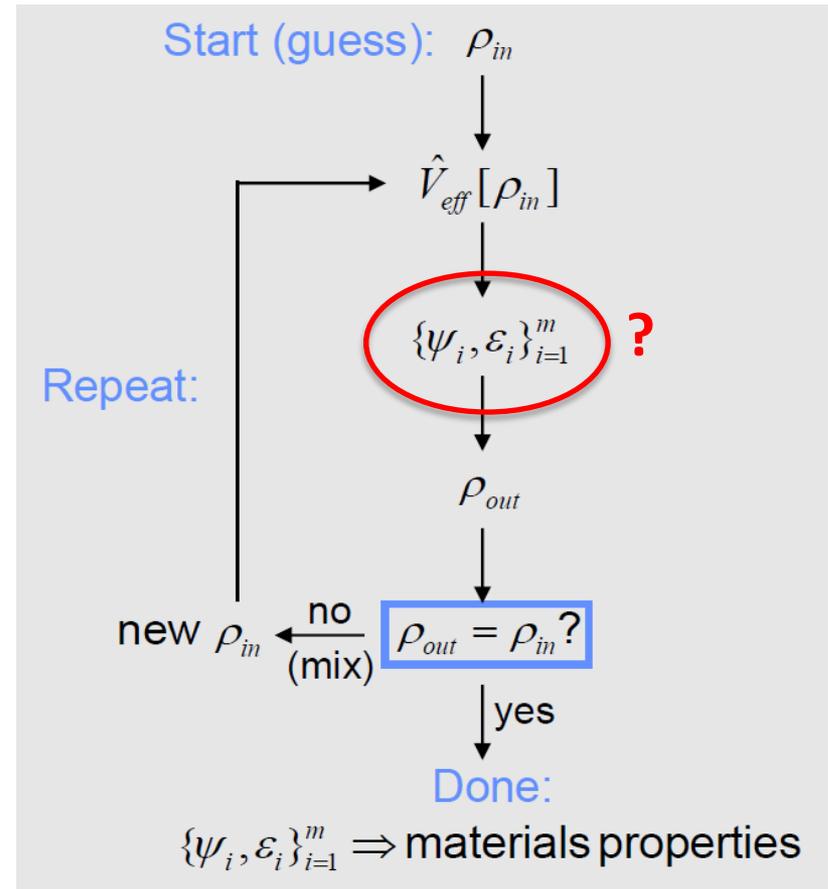
- Solve Kohn-Sham equations for electronic structure, compute quantum mechanical forces, move atoms, repeat – thousands to millions of times

Kohn-Sham equations

$$\begin{aligned} -\frac{1}{2}\nabla^2\psi_i(\mathbf{x}) + \hat{V}_{\text{eff}}\psi_i(\mathbf{x}) &= \varepsilon_i\psi_i(\mathbf{x}), \\ \hat{V}_{\text{eff}} &= V_I^\ell + \hat{V}_I^{nl} + V_H + V_{xc}, \quad (\text{Schrödinger}) \\ V_I^\ell &= \sum_a V_{I,a}(\mathbf{x}), \\ \hat{V}_I^{nl}\psi_i &= \sum_a \int d\mathbf{x}' V_{I,a}^{nl}(\mathbf{x}, \mathbf{x}')\psi_i(\mathbf{x}'), \\ V_H &= -\int d\mathbf{x}' \frac{\rho_e(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}, \quad (\text{Poisson}) \\ V_{xc} &= V_{xc}(\mathbf{x}; \rho_e), \\ \rho_e &= -\sum_i f_i \psi_i^*(\mathbf{x})\psi_i(\mathbf{x}), \end{aligned}$$

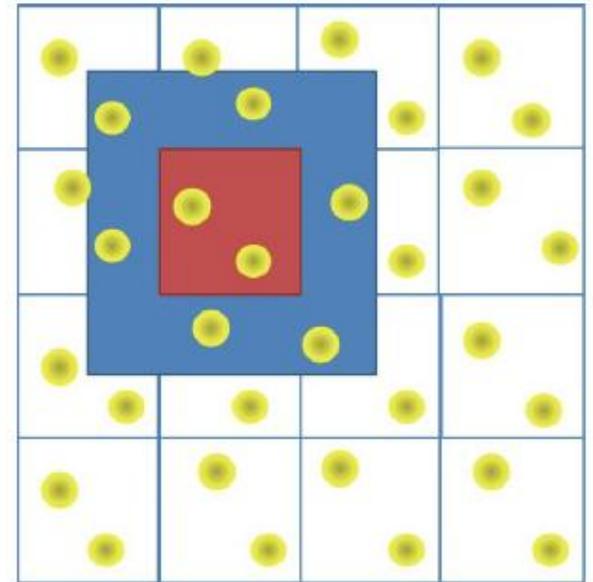
~ 10⁴ atoms, more eigenfunctions

Self-consistent field (SCF) solution process



What's new: releasing constraint of continuity

- DG framework allows solving the Kohn-Sham equations in a discontinuous basis
- Because basis can be discontinuous, can possess number of desirable properties simultaneously:
 - **Efficient** (few tens of DOF/atom)
 - **Systematically improvable**
 - **Strictly local**: identically zero outside prescribed subdomain, zero overlap across subdomains
 - **Orthonormal**: standard eigenproblem, well-cond.
- How?
 - Partition domain into subdomains (elements)
 - Solve Kohn-Sham equations in each element
 - Basis is union of local Kohn-Sham solutions



Solve large N -atom problem in highly efficient basis of $O(N)$ local Kohn-Sham solutions

DG formulation

- Discontinuity is accommodated by surface (“flux”) terms [1]
- Kohn-Sham Hamiltonian becomes

$$H_{DG}(k', j'; k, j) = \frac{1}{2} \langle \nabla u_{k', j'}, \nabla u_{k, j} \rangle_{\mathcal{T}} + \alpha \langle [[u_{k', j'}]], [[u_{k, j}]] \rangle_{\mathcal{S}} - \frac{1}{2} \langle [[u_{k', j'}]], \{ \{ \nabla u_{k, j} \} \} \rangle_{\mathcal{S}}$$

$$- \frac{1}{2} \langle \{ \{ \nabla u_{k', j'} \} \}, [[u_{k, j}]] \rangle_{\mathcal{S}} + \langle u_{k', j'}, V_{\text{eff}} u_{k, j} \rangle_{\mathcal{T}} + \sum_{\ell} \gamma_{\ell} \langle u_{k', j'}, b_{\ell} \rangle_{\mathcal{T}} \langle b_{\ell}, u_{k, j} \rangle_{\mathcal{T}}$$

\mathcal{T} = elements

\mathcal{S} = element surfaces

$u_{k, j}$ = j th basis function in k th element

$\{ \{ \cdot \} \}$ and $[[\cdot]]$ = average and jump operators across surfaces

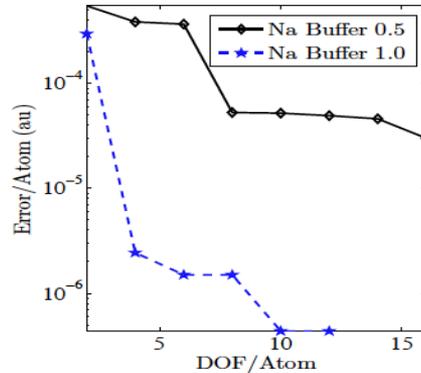
- Kohn-Sham equations: $H_{DG} c_i = \varepsilon_i c_i$
- Wavefunctions: $\psi_i = \sum_{E_k \in \mathcal{T}} \sum_{j=1}^{J_k} c_{i; k, j} u_{k, j}$

- Density: $\rho = \sum_{E_k \in \mathcal{T}} \sum_{i=1}^N \left| \sum_{j=1}^{J_k} c_{i; k, j} u_{k, j} \right|^2$

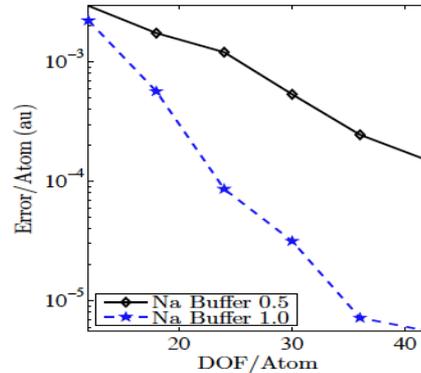
- Energy: $E_{\text{tot}} = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|} dx dy + \int \epsilon_{\text{xc}}[\rho(x)] dx - \int \epsilon'_{\text{xc}}[\rho(x)] \rho(x) dx$

Initial results

- Total energies converged to $< 1e-3$ Ha/atom absolute error with **15 basis funcs/atom**

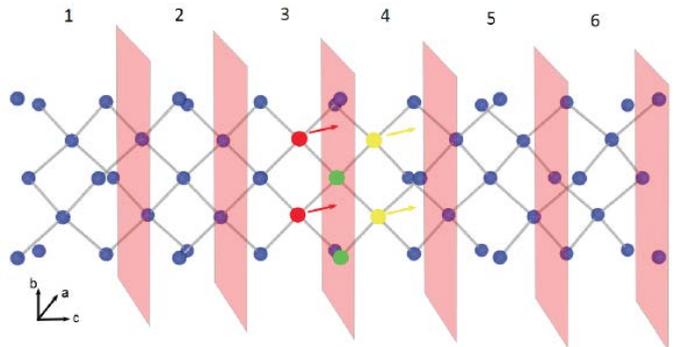


(a) Quasi-1D Na

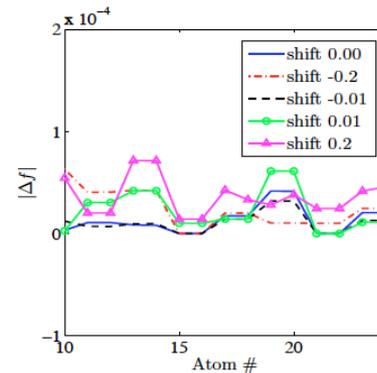


(b) Bulk 3D Na

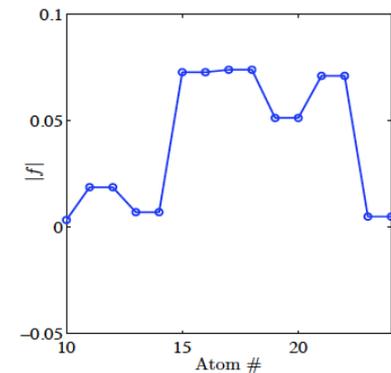
- Forces converged to $< 1e-4$ Ha/au absolute error with **15 basis funcs/atom**



Si: random displacements, series of translations



(a) Error of force



(b) Magnitude of force

- Largest system so far: **4,392 atoms** on 2,196 cpus by direct diagonalization using element orbitals [1]

What else is new: PEXSI

- Solving for Kohn-Sham wavefunctions of N atom system scales as $O(N^3)$
- Solve for density directly instead

$$\rho(x) = \text{diag} \left(f_{\beta}(\hat{H}[\rho(x)] - \mu\delta(x, x')) \right)$$

\hat{H} = Hamiltonian, μ = chemical potential, $f_{\beta}(x) = 2/(1 + e^{\beta x})$
 $\beta = 1/k_B T$, k_B = Boltzmann constant, T = temperature

- Need efficient approximation of Fermi function \rightarrow **Pole expansion** [1]

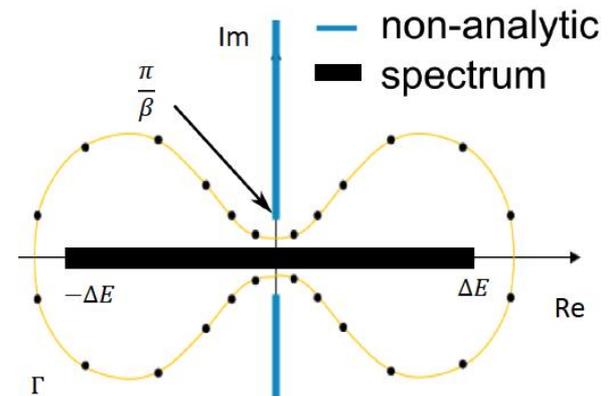
$$f_{\beta}(\varepsilon - \mu) \approx \Im \sum_{l=1}^P \frac{\omega_l^p}{\varepsilon - (z_l + \mu)}$$

$z_l, \omega_l^p \in \mathbb{C}$ are complex shifts and weights

- Need efficient inversion
- Need only diagonal \rightarrow **Selected Inversion** [2]
- \rightarrow **Pole Expansion and Selected Inversion (PEXSI)**

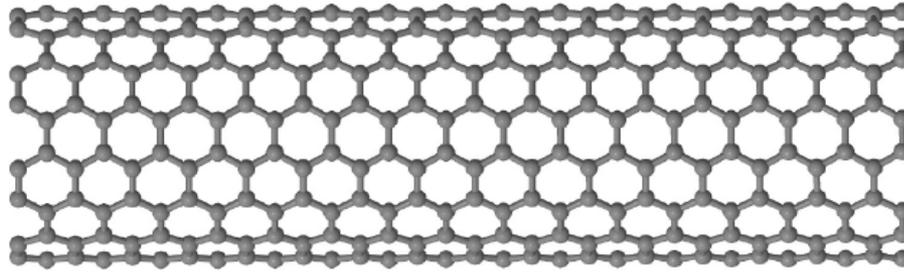
- **No need to compute eigenfunctions or eigenvalues**

- **Scaling $O(N)$ for quasi-1D systems; $O(N^2)$ for metallic 3D**



Initial results

- Metallic carbon nanotube, CNT (8,8), 512 atoms, atomic orbital basis [1]



- Accuracy of expansion at $T = 300\text{K}$

# Poles	$E_{\text{PEpSI}} - E_{\text{ref}}$ (eV)	MAE Force (eV/Angstrom)
20	5.868351108	0.400431
40	0.007370583	0.001142
60	0.000110382	0.000026
80	0.000000360	0.000002

- Largest system: **10,240 atoms**, 97 sec per pole (one SCF iteration) on a single processor

[1] Lin, Chen, Yang, He, 2012

SCF iterations

- Standard SCF convergence acceleration methods such as Anderson's method can show poor convergence for metallic systems, and strong temperature and system-size dependence
- New **elliptic preconditioner** [1] has been shown to effectively address both low-temperature and system-size issues, for metals and insulators alike

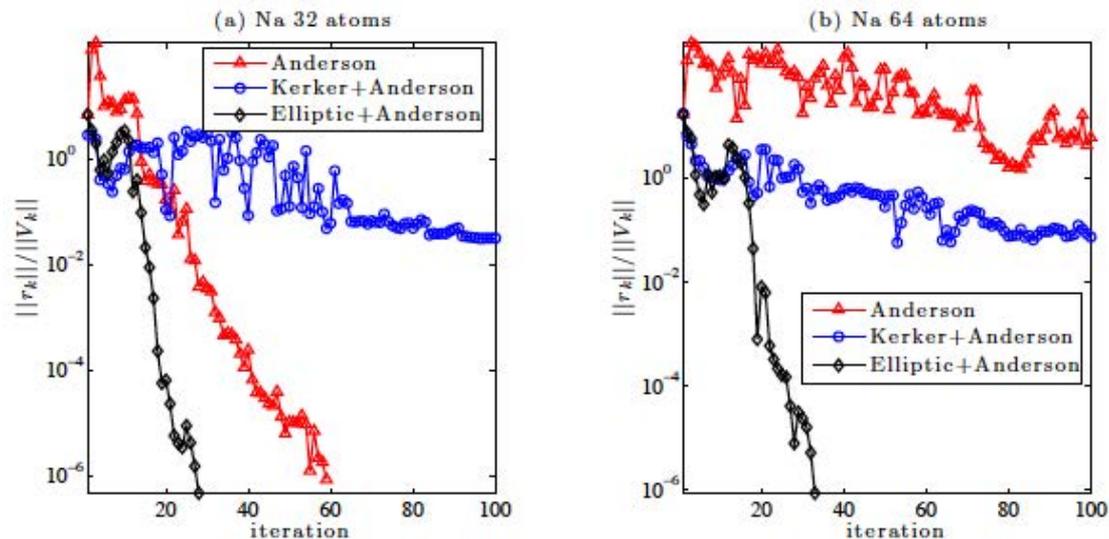


Fig. 6.6: The convergence of the Anderson's method, the Anderson's method with the Kerker preconditioner, and the Anderson's method with the elliptic preconditioner for quasi-1D Na systems with a large vacuum region with 32 Na atoms (a) and 64 Na atoms (b).

Parallelization

- Currently DG-KS parallelized over elements: MPI
- PEXSI serial
- To get to massive parallelism, will exploit multiple levels afforded by DG-PEXSI
 - ***k*-points**
 - **Poles**
 - **Elements**
 - **Quadrature points** (or other subdomains) within elements
- MPI or MPI/OpenMP hybrid



Summary

- **Goals:**
 - Develop new DG electronic structure method to accomplish QMD on unprecedented scales
 - Apply to understand structure and dynamics of electrolyte/SEI/anode systems in Li-ion cells
 - Make resulting new method/code available to community
- **So far:**
 - **DG-Kohn-Sham** method/code: $O(N^3)$, > **4,000 atoms SCF**, total energies and forces with planewave accuracy, parallelized over elements
 - **AO-PEXSI** method/code: $O(N)$ to $O(N^2)$, > **10,000 atoms SCF**, total energies and forces in agreement with $O(N^3)$ diagonalization, serial
- **To do:**
 - **DG-PEXSI**: $O(N)$ to $O(N^2)$, > **10,000-atom QMD**, total energies and forces with planewave accuracy; parallelized over k -points, poles, elements, intra-element; > **100,000 cpu**
 - **Apply** to electrolyte/SEI/anode systems of increasing complexity as methods/codes permit, 1,000 to > 10,000 atoms; understand structure/dynamics, compute key parameters
 - Document and distribute

